<Division of Synthetic Chemistry> Structural Organic Chemistry

Division of Synthetic Chemistry
- Structural Organic Chemistry -

http://hydrogen.kuicr.kyoto-u.ac.jp/KomatsuJ.html

Prof
KOMATSU, Koichi
(D Eng)

Assoc Prof
KITAGAWA, Toshikazu
(D Eng)

Assist Prof
NISHINAGA, Tohru
(D Eng)

Assist Prof
MURATA, Yasujiro
(D Eng)

PD
MORI, Sadayuki
(D Eng)

PD
ISHIDA, Shintaro
(D Sc)

PD
NOGITA, Rika
(D Sc)

PD
GAO, Yunyan
(D Sc)

PD
MINEGISHI, Shynya
(Ph D)

Students

LEE, Yangsoo (D3)
OGAWA, Kohei (D3)
MIYATA, Yasuo (D2)
MURATA, Michihisa (D2)
YAMAZAKI, Daisuke (D1)
MASAOKA, Naoki (M2)
UTO, Takayuki (M2)
YAMAZAKI, Tetsuya (M2)
TERAYAMA, Miki (M1)
MAEDA, Shuhei (M1)
MATSUBARA, Hiroaki (M1)
TANINO, Nobuhide (UG)
YOSHIDA, Ryohei (UG)

Scope of Research

Fundamental studies are being conducted for creation of new functional materials with novel structures and properties. The major subjects are: synthetic and structural studies on novel cyclic π-conjugated systems, particularly the positively charged species stabilized by σ–π interaction; synthesis of new redox-active and supramolecular π-systems; organochemical transformation of fullerenes C_{60} and C_{70}, specifically the synthesis of open-cage fullerene derivatives and introduction and encapsulation of small molecules in the fullerene cage; generation of alkylated C_{60} and C_{70} cations and their application for the synthesis of functional materials.

Research Activities (Year 2004)

Presentations

Organic Functionalization of C_{60} Toward Synthesis of Endohedral Fullerene, Komatsu K, Murata Y, Murata M, The 205th Meeting of The Electrochemical Society, 12 May, San Antonio, USA.

Alkylated Fullerenyl Cations: Their Generation, Isolation, and Stability, Kitagawa T, Lee Y, Masaoka N, Komatsu K, 17th IUPAC Conference on Physical Organic Chemistry, 18 August, Shanghai, P. R. China.

Sterically Segregated Cationic Oligothiophenes, Nishinaga T, Yamazaki D, Wakamiya A, Komatsu K, 6th International Symposium on Functional π-Electron Systems, 14 June, Ithaca, USA.

Synthesis and Properties of Open-Cage Fullerene C_{70} Derivatives, Murata Y, Maeda S, Murata M, Komatsu K, The 205th Meeting of The Electrochemical Society, 12 May, San Antonio, USA.

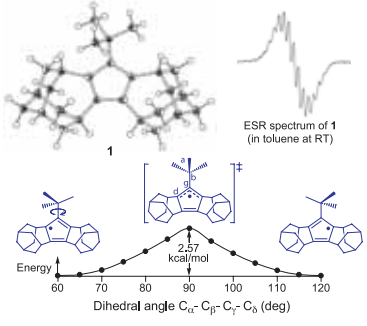
Grants

Komatsu K, Grant-in-Aid for Scientific Research (B), Development of Organic Synthetic Method for Endohedral Fullerenes, April 2004 - March 2006.

Kitagawa T, Grant-in-Aid for Scientific Research (C) (2), April 2004 - March 2006.

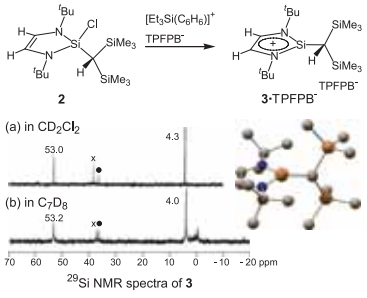
Spin-Localized Cyclopentadienyl Radical

A cyclopentadienyl radical **1**, incorporating annelated two homoadamantene frameworks and a *tert*-butyl group, was synthesized and isolated in stable, crystalline form by the single electron oxidation of the corresponding cyclopentadienyl anion with silver ion [1]. The X-ray structure clearly demonstrated distinct bond alternation in the cyclopentadienyl ring, suggesting that radical **1** has the characteristics of a spin-localized 2,4-cyclopentadien-1-yl radical. The two homoadamantene frameworks are nonequivalent in crystals at 100 K, while ESR spectra indicated that they are equivalent in toluene at room temperature due to rapid changes in conformation. These characteristics are fundamentally different from those previously reported for uniformly substituted cyclopentadienyl radicals, thus displaying the distinctive effect of annelation with rigid homoadamantene frameworks on the nature of cyclic π-conjugated systems.



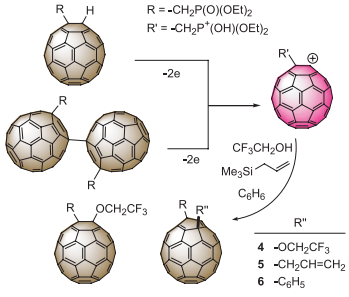
A New π-Conjugated Silylium Ion

Novel cationic silaaromatics, 2-silaimidazolium cation **3** was synthesized by chloride abstraction from the corresponding chlorosilane **2** with $[Et_3Si(benzene)]^+TPFPB^-$ ($TPFPB^-$ = tetrakis(pentafluorophenyl)borate) [2]. Cation **3** exists as a free silylium cation in solution due to bulky substituents on the five-membered ring. NMR spectroscopy and theoretical calculations showed the presence of aromaticity in 2-silaimidazolium ring, although its extent is smaller than that of the carbon analogue. The combined electronic effects of 6-π aromaticity and C–Si hyperconjugation are effective for stabilization of cation **3**.



Generation of Fullerenyl Cation $(EtO)_2P^+(OH)CH_2$-C_{60}^+

Fullerenes are typically electronegative molecules, and only a few examples are known for their cations. Nevertheless, a novel fullerenyl cation, $(EtO)_2P^+(OH)CH_2$-C_{60}^+, was quantitatively generated by simply dissolving RC_{60}-H or RC_{60}-$C_{60}R$ (R = $CH_2P(O)(OEt)_2$) in H_2SO_4. The cation was also generated in CD_2Cl_2 by the reaction of RC_{60}-H or RC_{60}-$C_{60}R$ with $(2,4\text{-}Br_2C_6H_3)_3N^{\cdot+}SbF_6^-$. The red-colored cation has a structure having an extra proton on a phosphoryl oxygen with the cationic center coordinated by the protonated oxygen. Various nucleophiles add to the cation selectively at 2- or 4- position, providing a new way to functionalize fullerenes [3].



[1] Kitagawa T, Ogawa K, Komatsu K, *J. Am. Chem. Soc.*, **2004**, *126,* 9930.
[2] Ishida S, Nishinaga T, West R, Komatsu K, *Chem. Commun.*, **2005**, 778.
[3] Murata Y, Cheng F, Kitagawa T, Komatsu K, *J. Am. Chem. Soc.*, **2004**, *126,* 8874.

Kitagawa T, CREST, Japan Science and Technology Agency, November 2002 - October 2007.

Nishinaga T, Grant-in-Aid for Young Scientists (A), April 2004 - March 2007.

Murata Y, Grant-in-Aid for Young Scientists (A), April 2004 - March 2007.

Murata Y, Komatsu K, Academic-Industrial Cooperative Research Fund, April 2004 - March 2005.

Awards

Nishinaga T, Konica Minolta Technology Center Award in Synthetic Organic Chemistry, Japan, Development of Molecular Wire Insulated by Rigid Carbon-Frameworks and Evaluation of Redox-Based Switching Properties, The Society of Synthetic Organic Chemistry, Japan, 18 February 2004.

Murata Y, The Chemical Society of Japan Award for Young Chemists, Novel Structural Transformation of Fullerene C_{60}, The Chemical Society of Japan, 27 March 2004.